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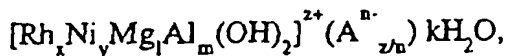
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(54) Title: CATALYST OBTAINABLE BY CALCINING A HYDROTALCITE-LIKE PRECURSOR AND ITS USE FOR THE PARTIAL OXIDATION OF METHANE



(I)

compound in which Al, and Rh and/or Ni cations are soluted, prepared from an (HT) precursor represented by the general formula (I): $[\text{Rh}_x\text{Ni}_y\text{Mg}_1\text{Al}_m(\text{OH})_2]^{2+}(\text{A}^{n-})_{z/n}\text{K}_2\text{H}_2\text{O}$, wherein A^{n-} is a silicate or a polysilicate anion, $0 \leq x \leq 0.3$; $0 \leq y \leq 0.9$; $0 \leq 1 \leq 0.9$; $0 \leq m \leq 0.5$; $x+y>0$; $0.5 \leq 1+y \leq 0.9$; $0 \leq k \leq 10$; $x+y+1+m=1$; and z is the total electrical charge of the cationic element. Use of a composition as catalyst of the partial oxidation of natural gas and/or light hydrocarbons ($\text{C}_2\text{-C}_4$) to synthesis gas and/or selective oxidations.

(57) Abstract: Composition characterized in that it essentially consists in a solid solution of a mixture of at least a Magnesium oxide type phase compound and at least a Magnesium silicate type phase com-

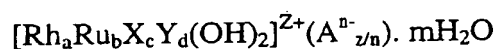
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CATALYST OBTAINABLE BY CALCINING A HYDROTALCITE-LIKE PRECURSOR AND ITS USE FOR THE PARTIAL OXIDATION OF METHANE

The present invention relates to a new catalysts for the partial oxidation of hydrocarbons.

The catalytic partial oxidation of hydrocarbons, natural gas or methane to synthesis gas has been processed for many years. While currently limited as an industrial process, the partial oxidation is of interest for the significant released heat and for the use of smaller reactors.

European patent application EP 0 725 038 discloses a material having a layered structure of hydrotalcite type in which rhodium is inside the interior of said structure which can be represented by the general formula :



wherein X and Y are divalent or trivalent metal cations,

$0 \leq a \leq 0,5$; $0 \leq b \leq 0,5$; $0,5 \leq c \leq 0,9$; $0 \leq d \leq 0,5$ and $a + b + c + d = 1$,

m is 0 or a positive integer,

A is a hydroxyl or any anion or anionic complex having n electrical charge.

z is the total electrical charge of the cationic component.

International patent publication WO 01/25142 discloses a catalyst obtained from an hydrotalcite type precursor containing nickel using steam and/or CO₂ in the reforming process.

International patent publication WO 01/53196 discloses a catalyst which consists in a refractory fibrous structure comprising a plurality of ceramic oxide fibres and at least one active catalyst element, chosen among Rh, Ni and Cr, supported on said fibrous structure. Such a catalyst claimed to resist thermal shock better than the conventional supported catalysts do.

International patent publication WO 01/28679 discloses a catalyst which consists in a mixture of at least two metal carbides metals (especially Mo, W, Cr) which optionally include an additional promoter and/or a catalyst support. It is claimed that no appreciable coking occurs, the catalyst desactivation is avoided or at least delayed, and this catalyst can be worked at the industrial level under better economical conditions than the conventional catalysts do.

However, none of the existing catalytic partial oxidation processes are able to reach a sufficient high conversion rate of reactant gas and the high selectivity of CO and H₂ reaction products can not be reached without using a large amount of rare and costly catalysts, or experiencing excessive coking of the catalyst or premature catalyst failure due to a lack of heat resistance and a mechanical instability of the catalyst on the support structure.

There is indeed a continuing need for new catalysts that are mechanically stable and that retain a high level of activity and selectivity to CO and H₂ products under conditions of high temperature, without excessive coking.

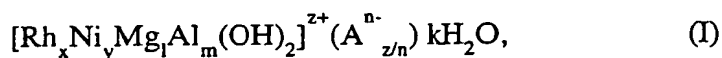
The inventors have found that the catalysts of the present invention overcome some of these drawbacks.

Accordingly, the present invention provides a composition characterized in that it essentially consists in a solid solution of a mixture of at least a magnesium oxide type phase compound and at least a magnesium silicate type phase compound in which Al, and Rh and/or Ni cations are soluted.

The precursor is a hydrotalcite-type structure and after calcination at 900°C two main phases are present : magnesium oxide type phase, a magnesium silicate type phase (forsterite-type), in which Al and the cation of the active phase (Rh and/or Ni) are soluted.

The catalysts useful in the process of this invention can be prepared from a precursor containing active metals of VIII group (Ni and/or Rh) and silicates as anions having a structure that is referred to as "hydrotalcite-like" (HT). Hydrotalcite-like compounds are anionic clays, that have a sheet-like structure. The sheets are separated by anions which balance the net positive charge of the sheets. In the context of the present invention, the anions of the anionic sheets are silicates or polysilicates and in the cationic sheets are present Ni or Rh, or a combination of those. The materials obtained by calcination of said Hydrotalcite-like compounds have high thermal resistance and are very stable. After an activation procedure, they are very active and do not show any carbon formation in the catalytic partial oxidation process.

More specifically, the catalyst of the present invention is prepared from an HT precursor represented by the general formula (I) :



wherein Aⁿ⁻ is mainly a silicate or a polysilicate anion ;

$$0 \leq x \leq 0.3 ;$$

$$0 \leq y \leq 0.9 ;$$

$$0 \leq l \leq 0.9 ;$$

$$0 \leq m \leq 0.5 ;$$

$$0 \leq k \leq 10 ;$$

$$x + y > 0 ;$$

$$0.5 \leq y + l \leq 0.9 ;$$

$$x + y + l + m = 1 ; \text{ and}$$

z is the total electrical charge of the cationic element.

In a preferred embodiment of the present invention,

$$0 \leq x \leq 0.1 ;$$

$$0 \leq y \leq 0.3 ;$$

$$0.3 \leq l \leq 0.8 ;$$

$$0.1 \leq m \leq 0.4 ;$$

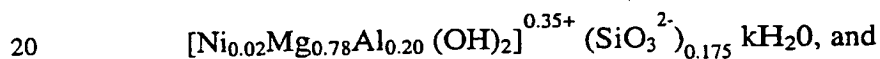
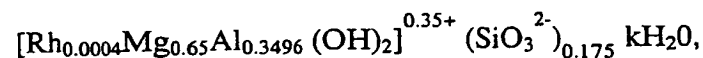
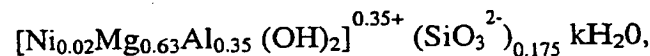
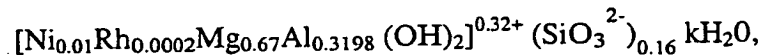
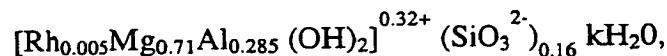
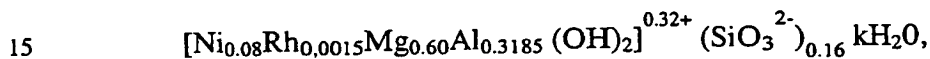
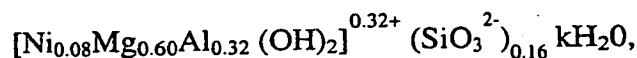
$$0 \leq k \leq 5 ;$$

$$x + y > 0 ;$$

$$0.6 \leq y + l \leq 0.8 ;$$

$$x + y + l + m = 1.$$

Among the above mentioned catalysts, the following compounds are the most preferred :



The composition according to the present invention is used in the reactions of reduction of nitrogen oxides, of hydroformulation, of hydrogenation of CO, CO₂ and mixtures thereof, of the conversion hydrocarbonaceous feedstocks such as natural gas or low-boiling liquid hydrocarbons into synthesis gas by catalytic partial oxidation.

The composition are generally used in temperature operating conditions within the range of 500°C to 1300°C, preferably between 600°C to 1100°C, in pressure operating condition within the range of 10⁵ Pa to 30 10⁵ Pa, preferably between 10⁵ Pa to 10 10⁵ Pa.

The composition are generally used in catalyst operating conditions which are any oxidant feed preferably pure oxygen, oxygen and inert gas mixture, such as nitrogen or argon, steam, carbon dioxide or a mixture of part or/and all of them.

The active phase of the catalyst can optionally be supported on classical catalytic supports such as alumina, zirconia, silicon carbide or magnesium oxide, in several forms, such as beads, pellets, or monoliths.

The composition according to the present invention is more specifically used :

as a catalyst of the partial oxidation of natural gas and/or light hydrocarbons (C₂-C₄) to synthesis gas and/or selective oxidations ;

as a catalyst of the steam and/or dry reforming of natural gas and/or light hydrocarbons (C₂-C₄) to synthesis gas and/or selective oxidations ;

as a catalyst of hydrogenation reaction ; or

as a catalyst of dehydrogenated oxydative reactions.

The following examples illustrate the present invention without limiting it.

Example 1 : Catalyst prepared from $[\text{Ni}_{0.08}\text{Mg}_{0.60}\text{Al}_{0.32}(\text{OH})_2]^{0.32+}(\text{SiO}_3^{2-})_{0.16} \cdot \text{kH}_2\text{O}$
(Ni8/Mg60/Al32)

A first solution is prepared by mixing 13.23 g of magnesium nitrate hexahydrate, 2.00 g of nickel (II) nitrate hexahydrate and 10.32 g of aluminium nitrate nonahydrate and by dissolving it in distilled water at the temperature of 60°C.

A second solution is prepared by dissolving 4.00 g of sodium silicate in water and at pH = 11.

Both solutions are simultaneously poured into distilled water, under strong stirring at 60°C and the resulting solution is brought to pH = 10.5 by adding 3 M NaOH. Stirring is continued for one hour, with temperature being constantly kept at 60°C. The precipitate is filtered off, washed with distilled water and dried overnight at 90°C, to form the catalyst precursor. The catalyst was obtained after calcination at 900°C during 15 hours.

The materials dried at 90°C and the catalyst were characterised by powder X-Ray Diffraction. Figure 1 represents this X Ray Diffraction graphs (XRD graph), and emphasizes that the precursor has an hydrotalcite- like structure while the main phases of the catalyst are

magnesium oxide type phase (figure 1 : □ MgO type) and magnesium silicate type phase (figure 1 : ● MgSiO₄ (forsterite type)). Al and Ni are inserted in these phases to form a solid solution.

On the XRD graph of the used catalyst of Figure 2 after partial oxidation, it can be observed that, besides the phase of the calcined sample, there is a Ni⁰ phase and a decrease of the intensity of the MgO type phase due to the reduction of Ni present in this phase (around 44 - 45 °2 Theta).

The surface area after calcination is 102 m²/g, while the surface area of the used catalyst is 108 m²/g, which confirms the thermal stability of the material.

10 **Example 2 : Catalyst prepared from [Ni_{0.08}Rh_{0.0015}Mg_{0.60}Al_{0.3185}(OH)₂]^{0.32+}(SiO₃)_{0.16}²⁻·kH₂O (Ni8/Rh0.15/Mg60/Al31.85)**

13.23 g of magnesium nitrate hexahydrate, 2.00 g of nickel (II) nitrate hexahydrate, 10.30 g of aluminium nitrate nonahydrate, 0.13 g of rhodium (III) nitrate solution (10% Rh) are dissolved in a beaker of distilled water at the temperature of 60°C. This solution was dropped simultaneously with 4.00 g of sodium silicate (diluted in water at pH 11) into distilled water under vigorous stirring at 60°C and keeping a pH of 10.5 by adding 3M NaOH. Stirring is continued for one hour, with temperature being constantly kept at 60°C.

The precipitate is filtered and washed with distillate water, then dried overnight at 90°C. The catalyst was obtained after calcination at 900°C for 15hr.

20 The precursor has an hydrotalcite-like structure analogously to the example 1 while Figure 3 represents the X Ray Diffraction graph (XRD graph) of the calcined sample, the main phases of which are magnesium oxide type phase (figure 1 : □ MgO type) and magnesium silicate type phase (figure 1 : ● MgSiO₄ (forsterite type)). Al and the active materials are inserted in these phases to form a solid solution.

25 On the XRD graph of the used catalyst of Figure 4, it can be observed, that besides the phase of the calcined samples, there is a Ni⁰ phase and a decrease of the intensity of the MgO type phase due to the reduction of Ni present in this phase. The reduced Rh present in low percentage is not visible in the used sample.

The surface area after calcination is 114 m²/g, while the surface area of used catalyst is 120 m²/g and the pore distribution before and after reaction is very similar and almost all the

porosity shows a pore radius comprised in the range from 10 to 200 Å, both confirming the thermal stability of the material.

Example 3 : Catalyst prepared from $[\text{Rh}_{0.005}\text{Mg}_{0.71}\text{Al}_{0.285}(\text{OH})_2]^{0.32+}(\text{SiO}_3^{2-})_{0.16}\cdot\text{kH}_2\text{O}$,

(Rh0.5/Mg71/Al28.5)

20.77 g of magnesium nitrate hexahydrate, 12.20 g of aluminium nitrate nonahydrate, 0.5 g of rhodium (III) nitrate solution (10% Rh) are dissolved in a beaker of distilled water at the temperature of 60°C. This solution was dropped simultaneously with a solution obtained dissolving 4.00 g of sodium silicate into distilled water at pH 11 under vigorous stirring at 60°C and keeping a pH of 10.5 by adding 3M NaOH.

Stirring is continued for one hour, with temperature being constantly kept at 60°C. The precipitate is filtered and washed with distilled water, then dried overnight at 90°C. The catalyst was obtained after calcination at 900°C for 15 hours.

Also in this case At X-Ray Diffraction the precursor presents an hydrotalcite-like structure while the main phases of the catalyst are: magnesium/oxide type phase, magnesium silicate type phase (forsterite type), with Al and Rh inserted in these phases to form solid solution.

The XRD graph of the used catalyst does not show any difference with the calcined sample since the Rh is present in low percentage as disperse Rh^0 , which is the active phase.

The surface area after calcination is 106 m²/g, while the surface area of the used catalyst is 110 m²/g, and the pore distribution before and after reaction is very similar and almost all the porosity shows a pore radius within the range from 10 to 200 Å, both confirming the thermal stability of the material.

The insertion of Rh decreases the possibilities of coke formation, increases the reaction rate and therefore, when Ni is present, keeps it in the reduced and active state.

The catalysts can be used in the production of synthesis gas from natural gas and light hydrocarbons (C₂-C₄) using : steam, CO₂, O₂ or other oxygen source.

The advantages of the invention are :

- a rather simple way to produce an high surface area oxide and silicate materials with a reducible element inside the structure ;
- an homogeneous distribution of the active metals inside the structure of the precursor ;

- an high surface area that allows after reduction a good dispersion of the metal particles ;
- a strong interaction metal/support ;
- an high thermal stability of the phases and of the surface area.

5 Catalytic partial oxydation process on catalysts according to the invention

After reduction of the catalysts under a mixture of N₂ and H₂ at 750°C, the materials were tested in partial oxidation of methane. The reduction is useful to have the catalyst in its maximum of activity without waiting for stabilisation and to avoid that part of the catalyst is still oxidized. The reduction "in situ" of Rh and Rh/Ni shows from the beginning the same
 10 conversion than the pre reduced catalysts. The tests were carried out in a fixed bed quartz microreactor of 8 mm of diameter, loaded with 500 mg in granules (20-30 mesh).

The tests were carried out at atmospheric pressure in three different conditions of feed and space velocity expressed as the gas hourly space velocity, (GHSV) measured at 25°C, using two different oven temperatures (500°C and 750°C). The reaction products were analysed by gas
 15 chromatography.

The results with the catalyst of example 1 (Ni8/Mg60/Al32), are reported in the following table and in figure 5 for what concern the duration tests.

CH ₄ /O ₂ /He (v/v)	Temperature (°C)	GHSV (h ⁻¹)	Time on stream (day)	CH ₄ Conversion (%)	CO Selectivity (%)	H ₂ Selectivity (%)
2/1/20	500	54000	0	63	55	88
2/1/20	500	54000	7	65	58	84
2/1/4	750	30000	0	89	95	98
2/1/1	750	125000	0	92	97	96
2/1/1	750	125000	7	92	97	97

Table 1 : Catalytic Partial Oxydation on Ni8/Mg60/Al32 catalyst

20 The conversion of oxygen was complete in the whole series of catalytic tests. The catalyst is very active also at low reaction temperature using diluted feed (oven temperature 500°C and feed ratio CH₄/O₂/He = 2/1/20 v/v). In severe industrial reaction conditions (high temperature

and concentrated feed mixture), the catalyst is very active and selective and shows an high stability.

The used catalyst was characterised by powder XRD and the patterns were similar to those of the fresh materials. The only difference was the presence of the peaks of a metallic nickel phase with small crystallites (see figure 2). The active phase is therefore the metal (Rh and/or Ni) obtained by reducing the calcined samples. The surface area of the used catalyst was 108 m²/g, confirming the thermal stability of the material also after 7 days on stream at a reaction temperature of about 900°C.

The catalytic results of duration tests on the catalysts of example 2, (Ni8/Rh0.15/Mg60/Al31.5) and example 3 (Rh0.5/Mg71/Al28.5), are collected in Figures 6 and 7. The test conditions for the catalytic partial oxidation process are similar as the experimental parameters described in table 1.

The conversions of oxygen were complete in the whole series of catalytic tests. The catalysts are very active also at low reaction temperature using diluted feed (oven temperature 500°C and feed ratio CH₄ / O₂ / He = 2 / 1 / 20 v/v).

In severe industrial reaction conditions (high temperature and concentrated feed mixture) the catalysts are very active and selective and shows an high stability.

Comparison for Catalytic Partial Oxidation between a catalyst according to the invention and a commercial catalyst

The results on the catalyst of example 1 (Ni8/Mg60/Al32 ; table 1, figure 5) were compared with those of a commercial catalysts Rh (0.1 % by weight) on α - Al₂O₃ calcined at 900 °C (same experimental conditions as described in table 1).

The results of the duration tests Rh (0.1%wt) on α - Al₂O₃, are reported in figure 8 and summarised in table 2.

CH ₄ /O ₂ /He (v/v)	Temperature (°C)	GHSV (h ⁻¹)	Time on stream (day)	CH ₄ Conversion (%)	CO Selectivity (%)	H ₂ Selectivity (%)
2/1/20	500	54000	0	50	60	94
2/1/20	500	54000	7	49	59	93
2/1/4	750	30000	0	87	96	95
2/1/1	750	125000	0	88	96	93
2/1/1	750	125000	7	87	95	93

Table 2 : Catalytic Partial Oxidation on a commercial catalyst Rh (0.1 % wt / α - Al₂O₃)

**Example 4: Catalyst prepared from $[\text{Ni}_{0.01}\text{Rh}_{0.0002}\text{Mg}_{0.67}\text{Al}_{0.3198}(\text{OH})_2]^{0.32+}(\text{SiO}_3^{2-})_{0.16}\cdot\text{kH}_2\text{O}$,
(Ni₁Rh_{0.02}Mg₆₇Al_{31.98})**

19.68 g of magnesium nitrate hexahydrate [Mg(NO₃)₂·6H₂O (99%)], 13.88 g of aluminium nitrate nonahydrate [Al(NO₃)₃·9H₂O (98%)], 0.33 g of nickel (II) nitrate hexahydrate [Ni(NO₃)₂·6H₂O (99%)] and 0.023 g of rhodium (III) nitrate solution (10% Rh) were dissolved in 57 ml of H₂O.

5.25 g of a 27 % w/w solution of SiO₂·NaOH were added to 118 ml of H₂O, and kept under magnetic stirring at 50-60°C.

The aqueous solution (2 M) of the metals nitrates was dropped into the silicates solution maintaining the pH between 10 and 11, by adding of 3M NaOH and the temperature at 50-60°C. The resulting solution was kept under stirring for 45 minutes and then filtered and washed with hot water (60°C). The hydrotalcite was dried at 100°C overnight and calcined at 900°C for 12 h. The XRD graph of the calcined sample the reflection of the Mg₂SiO₄ phase (*) and the (Mg/Ni/Rh)O phase (+).

The surface area before calcination was 136 m²/g, while after calcination, it was 87 m²/g.

**Example 5 : Catalyst prepared from $[\text{Ni}_{0.02}\text{Mg}_{0.63}\text{Al}_{0.35}(\text{OH})_2]^{0.35+}(\text{SiO}_3^{2-})_{0.175}\cdot\text{kH}_2\text{O}$,
(Ni₂Mg₆₃Al₃₅)**

9.50 g of magnesium nitrate hexahydrate [Mg(NO₃)₂·6H₂O (99%)], 25.26 g of aluminium nitrate nonahydrate [Al(NO₃)₃·9H₂O (98%)], 0.62 g of nickel (II) nitrate hexahydrate [Ni(NO₃)₂·6H₂O (99%)] were dissolved in 52 ml of H₂O.

9.55 g of a 27 % w/w solution of SiO₂·NaOH were added to 214 ml of H₂O, and kept under magnetic stirring at 50-60°C.

The aqueous solution (2 M) of the metals nitrates was dropped into the silicates solution

maintaining the pH between 10 and 11, by adding of 3M NaOH and the temperature at 50-60°C. The resulting solution was kept under stirring for 45 minutes and then filtered and washed with hot water (60°C). The hydrotalcite was dried at 100°C overnight and calcined at 900 °C for 12 h.

The surface area before calcination was 118 m²/g, while after calcination, it was 86 m²/g.

**Example 6 : Catalyst prepared from $[\text{Rh}_{0.0004}\text{Mg}_{0.65}\text{Al}_{0.3496}(\text{OH})_2]^{0.35+}(\text{SiO}_3^{2-})_{0.175}\cdot\text{kH}_2\text{O}$,
($\text{Rh}_{0.04}\text{Mg}_{65}\text{Al}_{34.96}$)**

19.10 g of magnesium nitrate hexahydrate [$\text{Mg}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ (99%)], 15.18 g of aluminium nitrate nonahydrate [$\text{Al}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$ (98%)] and 0.0467g of rhodium (III) nitrate solution (10% Rh) a solution 10 wt % of $\text{Rh}(\text{NO}_3)_3$ were dissolved in 57 ml of H_2O .

5.74 g of a 27 % w/w solution of $\text{SiO}_2\cdot\text{NaOH}$ were added to 129 ml of H_2O , and kept under magnetic stirring at 50-60°C.

The aqueous solution (2 M) of the metals nitrates was dropped into the silicates solution maintaining the pH between 10 and 11, by the adding 3M NaOH and the temperature at 50-60 °C. The resulting solution was kept under stirring for 45 minutes and then filtered and washed with hot water (60°C). The hydrotalcite was dried at 100°C overnight and calcined at 900°C for 12 h. The XRD analysis showed the reflection of the Mg_2SiO_4 and (Mg/Rh)O phases.

The surface area before calcination was 262 m²/g, while after calcination, it was 88 m²/g.

**Example 7 : Catalyst prepared from $[\text{Ni}_{0.02}\text{Mg}_{0.78}\text{Al}_{0.20}(\text{OH})_2]^{0.35+}(\text{SiO}_3^{2-})_{0.175}\cdot\text{kH}_2\text{O}$,
($\text{Ni}_2\text{Mg}_{78}\text{Al}_{20}$)**

23.42 g of magnesium nitrate hexahydrate [$\text{Mg}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ (99%)], 8.88 g of aluminium nitrate nonahydrate [$\text{Al}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$ (98%)], 0.68 g of nickel (II) nitrate hexahydrate [$\text{Ni}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ (99%)], were dissolved in 58 ml of H_2O .

3.35 g of a 27 % w/w solution of $\text{SiO}_2\cdot\text{NaOH}$ were added to 76 ml of H_2O , and kept under magnetic stirring at 50-60°C.

The aqueous solution (2 M) of the metals nitrates was dropped into the silicates solution maintaining the pH between 10 and 11, by adding 3M NaOH and the temperature at 50-60 °C.

The resulting solution was kept under stirring for 45 minutes and then filtered and washed with hot water (60°C).

The hydrotalcite was dried at 100°C overnight and calcined at 900°C for 12 h. The XRD analysis showed the reflection of the Mg_2SiO_4 and (Mg/Ni)O phases.

The surface area before calcination was 71 m²/g, while after calcination, it was 86 m²/g.

Example 8 : Catalyst prepared from $[\text{Rh}_{0.0004}\text{Mg}_{0.80}\text{Al}_{0.1996}(\text{OH})_2]^{0.20+}(\text{SiO}_3^{2-})_{0.10}\text{kH}_2\text{O}$, $(\text{Rh}_{0.04}\text{Mg}_{80}\text{Al}_{19.96})$

24.39 g of magnesium nitrate hexahydrate $[\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (99%)], 8.99 g of aluminium nitrate nonahydrate $[\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (98%)] and 0.0485 g of rhodium (III) nitrate solution (10% Rh) were dissolved in 59 ml of H_2O .

3.41 g of a 27 % w/w solution of $\text{SiO}_2 \cdot \text{NaOH}$ were added to 77 ml of H_2O , and kept under magnetic stirring at 50-60°C.

The aqueous solution (2 M) of the metals nitrates was dropped into the silicates solution maintaining the pH between 10 and 11 by adding 3M NaOH and the temperature at 50-60°C.

The resulting solution was kept under stirring for 45 minutes and then filtered and washed with hot water (60°C).

The hydrotalcite was dried at 100°C overnight and calcined at 900°C for 12 h. The XRD analysis showed the reflection of the Mg_2SiO_4 and $(\text{Mg/Rh})\text{O}$ phases.

The surface area before calcination was 125 m^2/g , while after calcinations, it was 82 m^2/g .

Catalytic partial oxidation process on catalysts according to the invention

Test with example 4 ($\text{Ni}_1\text{Rh}_{0.02}\text{Mg}_{67}\text{Al}_{31.98}$)

The catalyst of example 4, was tested under catalytic partial oxidation conditions. The tests were carried out using the following gas mixtures :

methane/oxygen/helium 2/1/20 (v/v) at 500°C and 750°C (residence time = 0.065 s) ;
methane/oxygen/helium 2/1/4, 2/1/1 and 4/2/2 (v/v) at 750°C (residence time for 2/1/4 = 0.065 s, residence time for 2/1/1 = 0.111 s and residence time for 4/2/2 = 0.056 s).

The methane conversion and CO and H_2 selectivity were high both at low (500°C) and high oven temperature. In particular, the catalytic performances of this catalyst reached the maximum with the methane/oxygen/helium 2/1/20 mixture at 750°C, showing very high value (98.7%). Using the harder reaction conditions the CH_4 conversion and the CO and H_2 selectivities were about constant and maintained high values.

CH ₄ /O ₂ /He	Oven T (°C)	CH ₄ conversion (%)	CO selectivity (%)	H ₂ selectivity (%)	T out (°C)	T max (°C)	Contact time (ms)
2/1/20	500	60,6	51,7	82,9	536	613	65
2/1/20	750	98,7	92,8	98,2	747	801	65
2/1/4	750	86,5	95,4	93,4	752	870	65
2/1/1	750	84,9	94,9	91,8	759	860	111
4/2/2	750	85,2	95,5	91,8	866	941	56
2/1/20-RET	500	57,4	49,4	78,2	530	630	65

Test with example 5 (Ni₂Mg₆₃Al₃₅)

The catalyst prepared in example 5, was tested under catalytic partial oxidation conditions. The tests were carried out using the following gas mixtures :

methane/oxygen/helium 2/1/20 (v/v) at 500°C and 750°C (residence time = 0.065 s) ;

methane/oxygen/helium 2/1/4, 2/1/1 and 4/2/2 (v/v) at 750°C (residence time for 2/1/4 = 0.065 s, residence time for 2/1/1 = 0.111 s and residence time for 4/2/2 = 0.056 s).

The catalyst which only contains Ni as an active phase, has a high activity at both 500°C and 750°C feeding the dilute mixture 2/1/20.

Using harder reaction conditions the CH₄ conversion was significantly lower than that of the bimetallic Rh/Ni catalyst.

No deactivation was observed at the end of the tests returning to the 2/1/20 mixture and the low temperature (500°C).

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CH ₄ /O ₂ /He	T oven (°C)	CH ₄ conversion (%)	CO selectivity (%)	H ₂ selectivity (%)	T out (°C)	T max (°C)	Contact time (ms)
2/1/20	500°C	53,9	46,3	74,7	530	598	65
2/1/20	750°C	95,2	93,9	93,0	745	789	65
2/1/4	750°C	76,6	90,7	89,5	755	889	65
2/1/1	750°C	74,5	88,1	87,7	743	905	111
4/2/2	750°C	79,3	93,1	90,0	851	936	56
2/1/20-RET	500°C	52,7	45,9	72,0	532	595	65

Test with example 6 ($\text{Rh}_{0.04}\text{Mg}_{65}\text{Al}_{34.96}$)

The catalyst prepared in example 6, was tested under catalytic partial oxidation conditions. The tests were carried out using the following mixtures :

methane/oxygen/helium 2/1/20 at 500 and 750°C (residence time = 0.065 s), and

methane/oxygen/helium 2/1/4, 2/1/1 and 4/2/2 (v/v) at 750°C (residence time for 2/1/4 = 0.065 s, residence time for 2/1/1 = 0.111 s and residence time for 4/2/2 = 0.056 s).

The catalyst, which only contains Rh as an active phase, was not reduced by the N_2/H_2 mixture feed for 12h at 750°C.

In fact feeding 2/1/20 mixture at 500°C and at 750°C, the catalytic performances are lower than that of the catalyst obtained in example 4 that only contains Ni.

Feeding more concentrated mixtures, the catalyst was reduced by the reaction mixture and the activity remarkably increased and was higher than the sample containing only Ni and lower than the one containing Rh/Ni as active phase.

$\text{CH}_4/\text{O}_2/\text{He}$	T oven (°C)	CH_4 conversion (%)	CO selectivity (%)	H_2 selectivity (%)	T out (°C)	T max (°C)	Contact time (ms)
2/1/20	500°C	8,7	0,0	0,0	531	531	65
2/1/20	750°C	67,9	74,8	78,5	760	829	65
2/1/4	750°C	79,9	89,3	90,0	759	883	65
2/1/1	750°C	81,5	92,6	90,7	755	873	111
4/2/2	750°C	81,7	93,1	90,7	775	943	56
2/1/20-RET	500°C	42,8	38,1	53,2	522	556	65

Test with example 7 ($\text{Ni}_2\text{Mg}_{78}\text{Al}_{20}$)

The catalyst prepared in example 7, was tested under catalytic partial oxidation conditions. The tests were carried out using the following mixtures :

methane/oxygen/helium 2/1/20 (v/v) at 500°C and at 750°C (residence time = 0.065 s),

and

methane/oxygen/helium 2/1/4, 2/1/1 and 4/2/2 (v/v) at 750°C (residence time for 2/1/4 = 0.065 s, residence time for 2/1/1 = 0.111 s and residence time for 4/2/2 = 0.056 s).

The catalyst has high activity at all reaction conditions. The increase of the ratio Mg/Al, with respect to the sample prepared as in example 5, had improved the methane conversion. No deactivation of the catalyst was observed coming back to initial conditions (500°C and 2/1/20 feed).

CH ₄ /O ₂ /He	T oven (°C)	CH ₄ conversion (%)	CO selectivity (%)	H ₂ Selectivity (%)	T out (°C)	T max (°C)	Contact time (ms)
2/1/20	500°C	56,5	48,1	79,1	543	610	65
2/1/20	750°C	96,1	90,2	98,2	753	778	65
2/1/4	750°C	82,1	93,4	91,0	770	819	65
2/1/1	750°C	80,5	92,4	89,8	761	832	111
4/2/2	750°C	80,0	93,6	90,6	805	877	56
2/1/20-RET	500°C	56,8	47,3	77,8	545	602	65

Test with example 8 (Rh_{0.04}Mg₈₀Al_{19.96})

The catalyst prepared in example 8, was tested under catalytic partial oxidation conditions.

- 5 The tests were carried out using the following mixtures :
methane/oxygen/helium 2/1/20 at 500°C and 750°C (residence time = 0.065 s), and methane/oxygen/helium 2/1/4, 2/1/1 and 4/2/2 at 750°C (residence time for 2/1/4 = 0.065 s, residence time for 2/1/1 = 0.111 s and residence time for 4/2/2 = 0.056 s).

10 The increase of the ratio Mg/Al, with respect to the sample prepared as in example 6, had improved the methane conversion.

The use of Rh as active phase instead of Ni improves the catalytic activity feeding the more concentrated mixtures (2/1/4, 2/1/1 and 4/2/2) at oven temperature of 750°C.

No deactivation of the catalyst was observed coming back to initial conditions (500°C and 2/1/20 feed).

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CH ₄ /O ₂ /He	T oven (°C)	CH ₄ Conversion (%)	CO Selectivity (%)	H ₂ Selectivity (%)	T out (°C)	T max (°C)	Contact time (ms)
2/1/20	500°C	49,4	50,3	62,5	532	643	65
2/1/20	750°C	88,5	89,3	92,7	751	825	65
2/1/4	750°C	84,3	93,4	93,0	764	888	65
2/1/1	750°C	84,0	93,2	92,4	757	878	111
4/2/2	750°C	85,5	94,4	95,7	770	965	56
2/1/20-RET	500°C	49,5	48,5	64,1	530	645	65

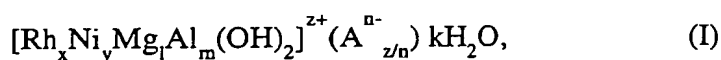
The advantages of the catalysts according to the invention are :

- a better conversion and selectivity levels,
- a better thermal stability in hard reaction conditions a high activity at short residence time, and
- 5 a lower cost when Ni is used to substitute partially or totally the Rh.

CLAIMS

1. Composition characterized in that it essentially consists in a solid solution of a mixture of at least a Magnesium oxide type phase compound and at least a Magnesium silicate type phase compound in which Al, and Rh and/or Ni cations are soluted.

2. Composition according to claim 1, prepared from an HT precursor represented by the general formula (I) :



wherein A^{n-} is a silicate or a polysilicate anion,

$$0 \leq x \leq 0.3 ;$$

$$0 \leq y \leq 0.9 ;$$

$$0 \leq l \leq 0.9 ;$$

$$0 \leq m \leq 0.5 ;$$

$$x + y > 0 ;$$

$$0.5 \leq l + y \leq 0.9 ;$$

$$0 \leq k \leq 10 ;$$

$$x + y + l + m = 1 ;$$

and z is the total electrical charge of the cationic element.

3. Composition according to claim 1, prepared from an HT precursor characterized in that in the formula (I),

$$0 \leq x \leq 0.1 ;$$

$$0 \leq y \leq 0.3 ;$$

$$0.3 \leq l \leq 0.8 ;$$

$$0.1 \leq m \leq 0.4 ;$$

$$x + y > 0 ;$$

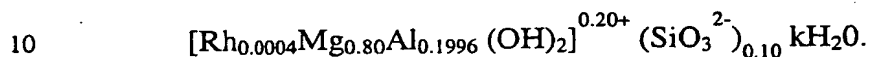
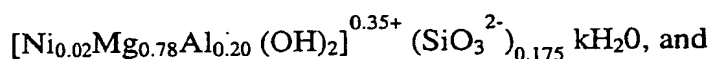
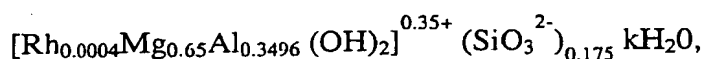
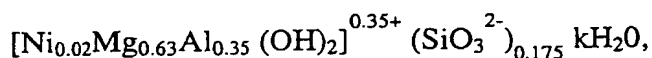
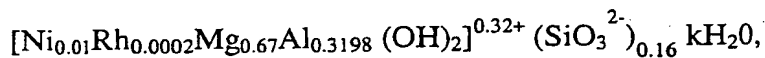
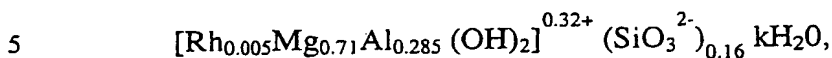
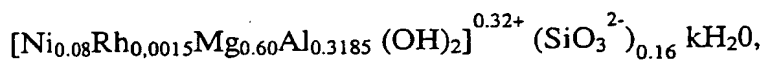
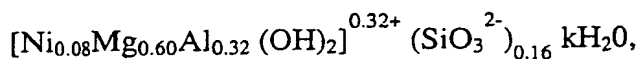
$$0.6 \leq l + y \leq 0.8 ;$$

$$0 \leq k \leq 5 ;$$

$$x + y + l + m = 1 ;$$

and z is the total electrical charge of the cationic element.

4. Composition according to claim 1 prepared from an HT precursor represented by one of the following formulas :



5. Method of synthesis of a composition according to any of claim 1 to 4, characterized in that it essentially consists in calcinating a anionic clays, that have an hydrotalcite-like wherein the positively charged sheets are separated by anions, preferably silicate anions or polysilicate anions, which balance the net positive charge of the sheets which contains Ni or Rh cations or a mixture of Ni and Rh cations.

6. Use of a composition according to any of claim 1 to 4, as catalyst of the partial oxidation of natural gas and/or light hydrocarbons ($\text{C}_2\text{-C}_4$) to synthesis gas and/or selective oxidations.

7. Use of a composition according to any of claim 1 to 4, as catalyst of the steam and/or dry reforming of natural gas and/or light hydrocarbons ($\text{C}_2\text{-C}_4$) to synthesis gas and/or selective oxidations.

8. Use of a composition according to any claim 1 to 4 which the operating catalyst conditions are in the range of 500 to 1300°C and preferably between 600 to 1100°C.

9. Use of a composition according to any claim 1 to 4 which the operating catalyst conditions are in the range of 10^5 Pa to $3 \cdot 10^6$ Pa and preferably between 10^5 Pa to 10^6 Pa.

10. Use of a composition according to any claim 1 to 8 which the operating catalyst conditions are any oxydant feed, preferably pure oxygen, oxygen and inert gas mixture, steam, carbon dioxide or a mixture of part or/and all of them.

11. Use of a composition according to any of claim 1 to 4 as catalyst of hydrogenation

reaction.

12. Use of a composition according to any of claim 1 to 4 as catalyst of oxidative dehydrogenation reactions.

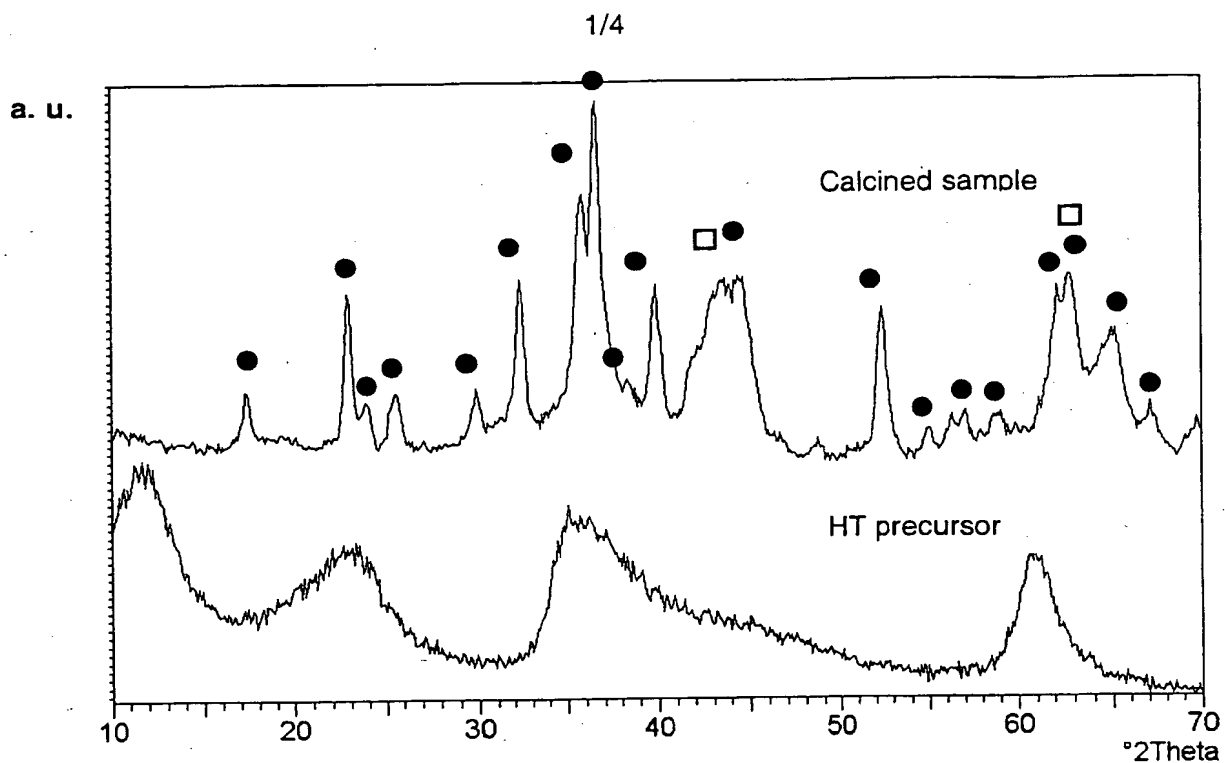


Figure 1

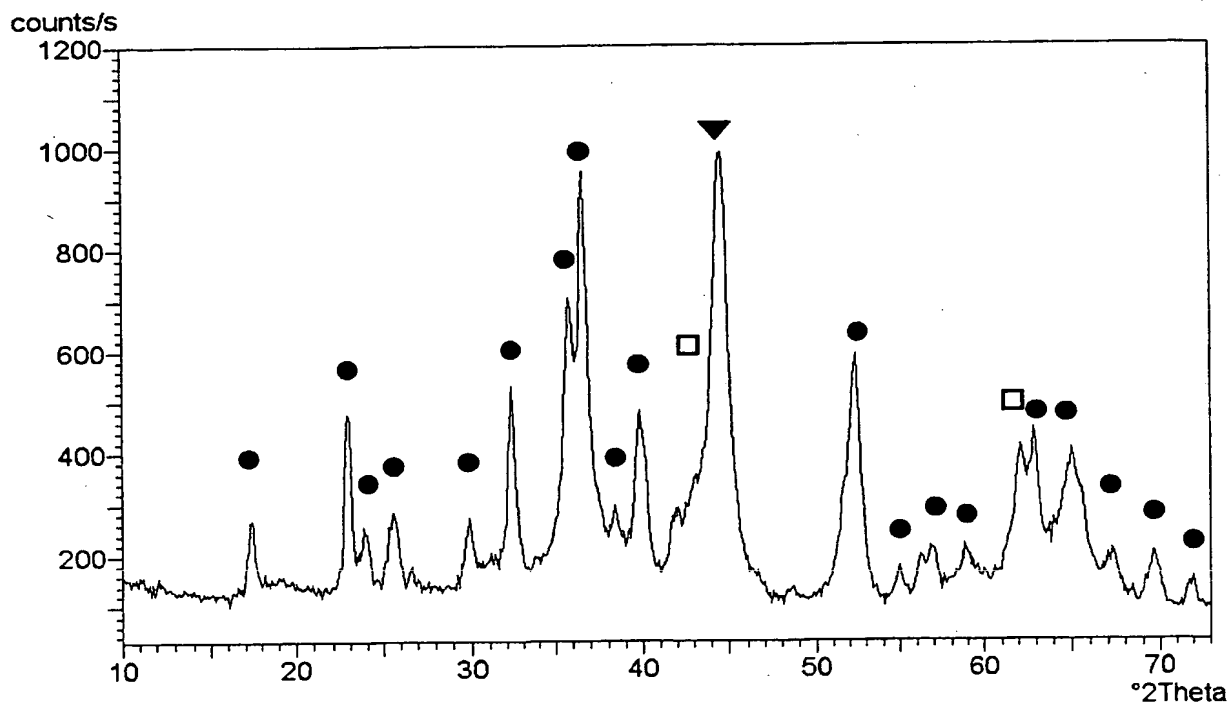


Figure 2

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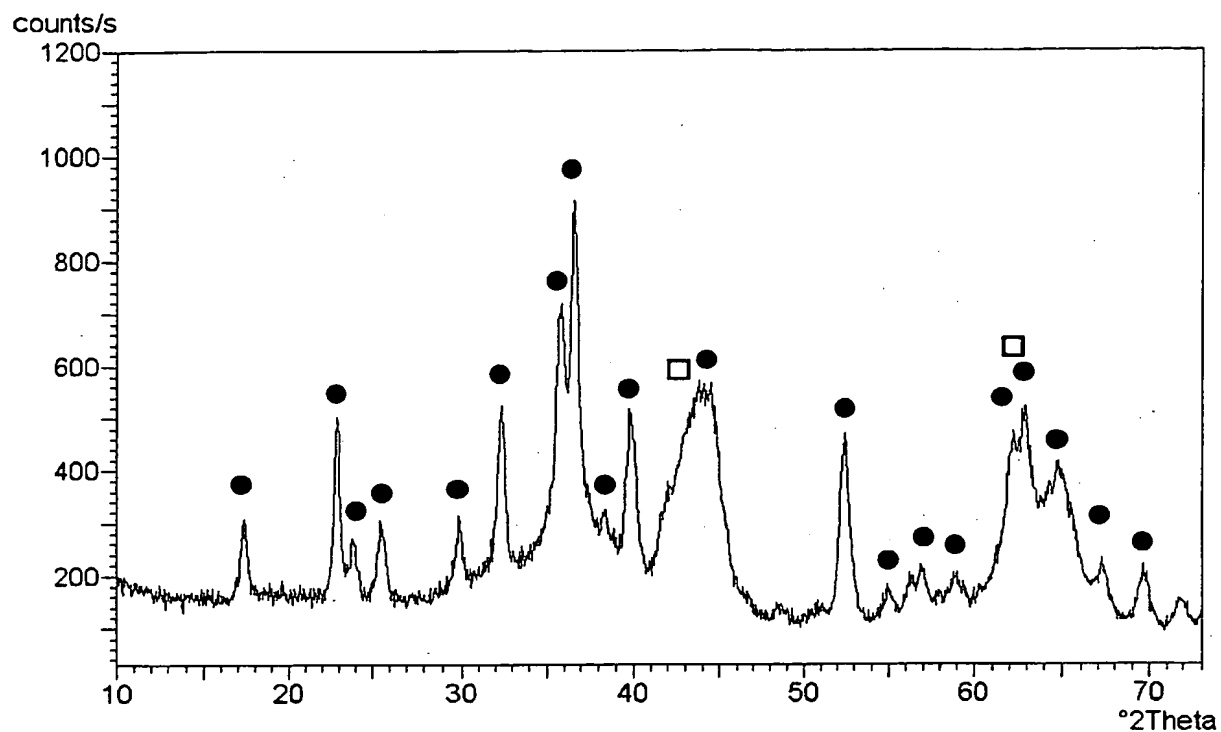


Figure 3

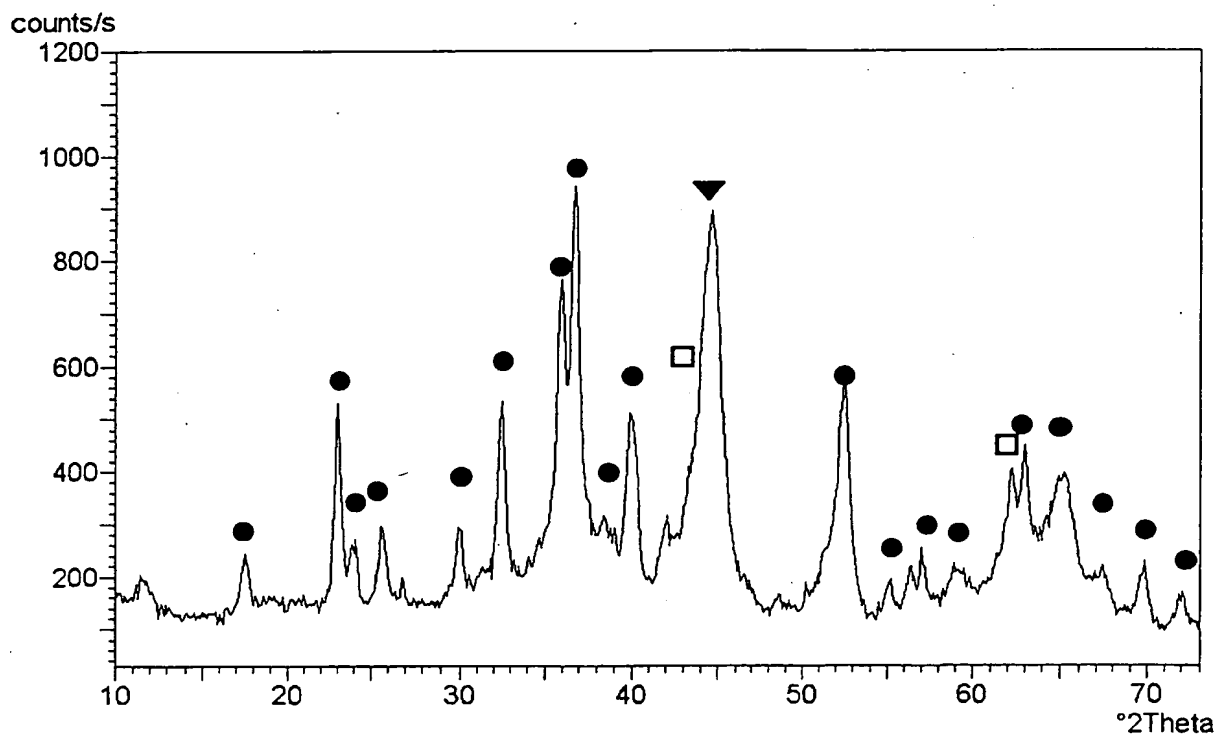


Figure 4

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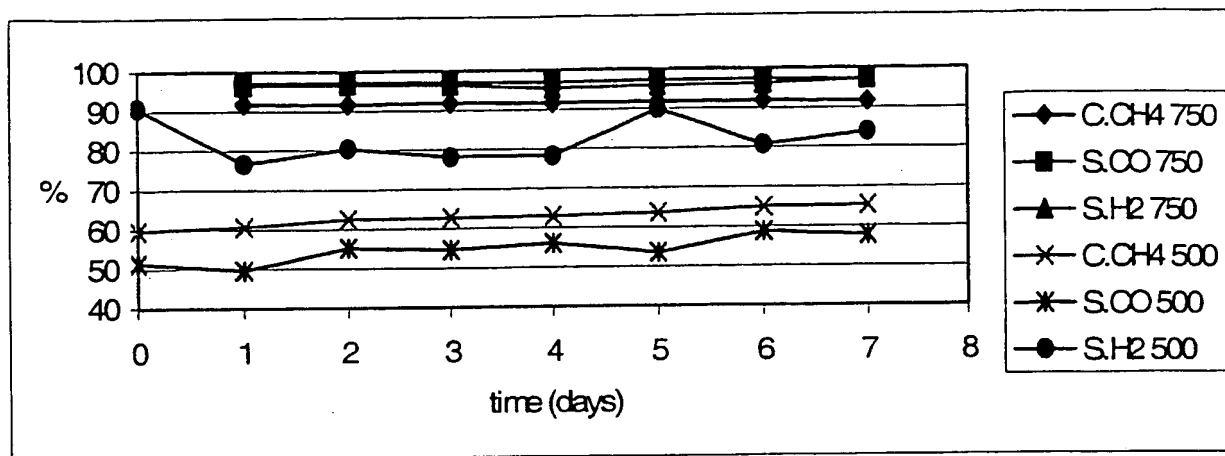


Figure 5: Result of stability test of $\text{Ni}_8/\text{Mg}_{60}/\text{Al}_{32}$ (load: 0.5g) performed at 500°C ($\text{CH}_4:2/\text{O}_2:1/\text{He}:20$) and 750°C ($\text{CH}_4:2/\text{O}_2:1/\text{He}:1$)

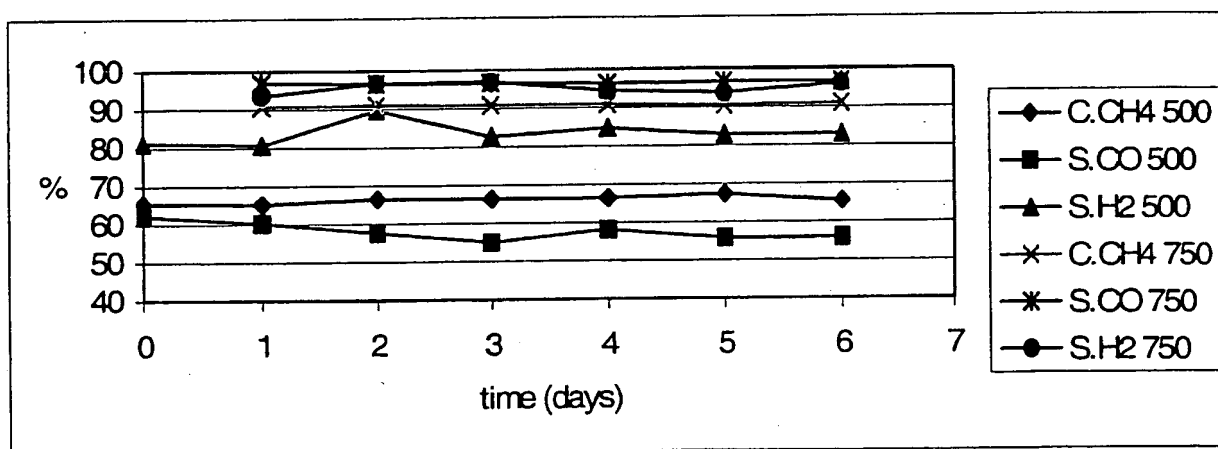


Figure 6: Result of durability test of $\text{Ni}_8/\text{Rh}_{0.15}/\text{Mg}_{60}/\text{Al}_{31.85}$ (load: 0.5g) performed at 500°C ($\text{CH}_4:2/\text{O}_2:1/\text{He}:20$) and 750°C ($\text{CH}_4:2/\text{O}_2:1/\text{He}:1$)

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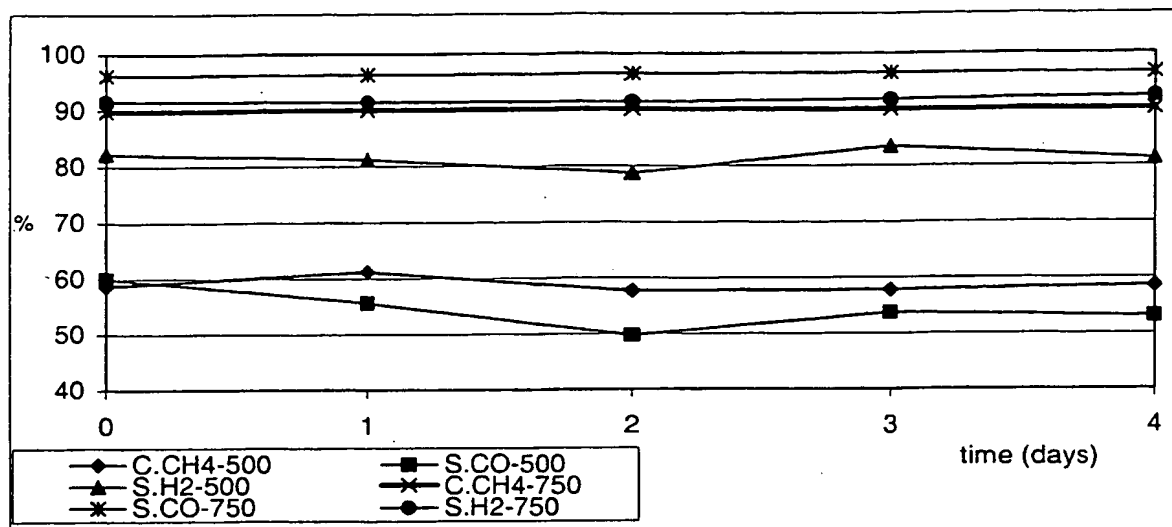


Figure 7 Result of durability test of $\text{Rh}_{0.5}/\text{Mg}_{71}/\text{Al}_{28.5}$ (load: 0.5g) performed at 500°C ($\text{CH}_4:2/\text{O}_2:1/\text{He}:20$) and 750°C ($\text{CH}_4:2/\text{O}_2:1/\text{He}:1$)

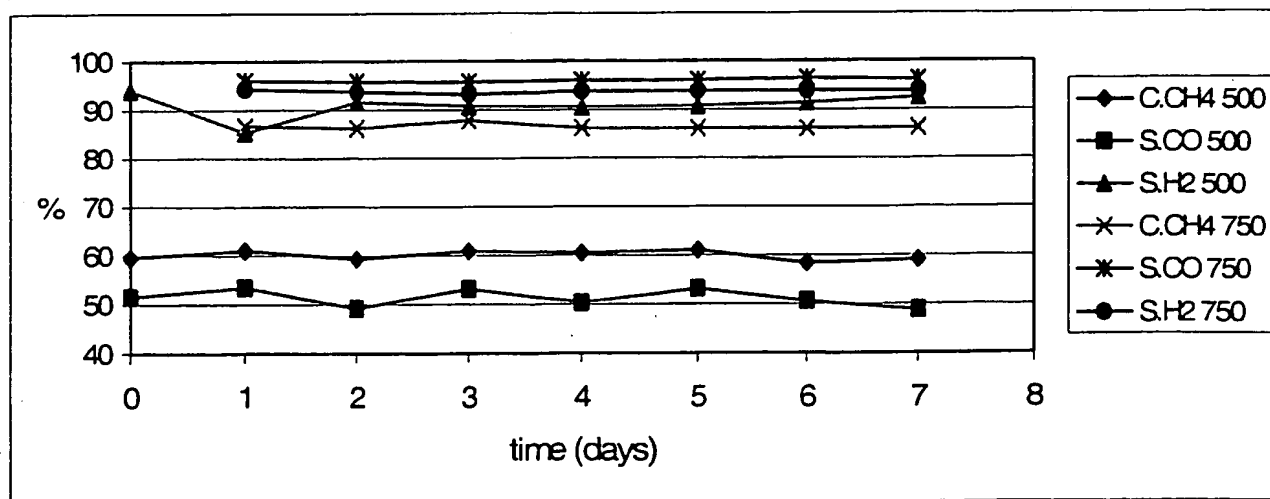


Figure 8. Deactivation test on the 0.1%Rh/ α - Al_2O_3 (load: 1.5g) performed at 500°C ($\text{CH}_4:2/\text{O}_2:1/\text{He}:20$) and 750°C ($\text{CH}_4:2/\text{O}_2:1/\text{He}:1$)

INTERNATIONAL SEARCH REPORT

Int. Application No
PCT/IB 03/01673

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 B01J35/00 B01J23/46 B01J23/755 B01J23/89 C01B3/40

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB 1 064 939 A (AZOTE OFFICE NAT IND) 12 April 1967 (1967-04-12) page 1, line 44 - line 72 page 2, line 30 - line 45 ----	1,6,7,9
X	US 4 217 295 A (FRIEDRICH HEINZ G ET AL) 12 August 1980 (1980-08-12) example 3 ----	1
X	EP 0 725 038 A (SNAM PROGETTI) 7 August 1996 (1996-08-07) cited in the application examples 1,2,7-9 page 3, line 2 - line 3 page 3, line 27 - line 48 ----- -/-	1-12

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

15 July 2003

Date of mailing of the international search report

29/07/2003

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INTERNATIONAL SEARCH REPORT

Int. Application No.

PCT/IB 03/01673

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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